

UPTAKE OF DICHROMATE FROM AQUEOUS SYSTEM USING Zn-Al-NO₃ HYDROTALCITE THROUGH ANION EXCHANGE

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Abstract

Chromium species, one of toxic pollutants in aqueous system particularly in the form of dichromate, is treated using an ion exchanger of Zn-Al-NO₃ hydrotalcite. Synthesis of Zn-Al-NO₃ hydrotalcite and its application as an anion exchanger to lower dichromate concentration has been done. Zn-Al-NO₃ hydrotalcite was prepared using stoichiometric method at a constant pH of 7 where hydrothermal treatment was added. Kinetics and mechanism of anion exchange of NO₃⁻ in Zn-Al-NO₃ hydrotalcite by dichromate anion and regeneration process were investigated. The products were characterized by XRD, FT-IR and atomic adsorption spectrophotometry. The initial Zn-Al-NO₃ hydrotalcite has chemical formula of Zn_{0.74}Al_{0.26}(OH)_{1.7}(NO₃)_{0.26}·0.27H₂O. Kinetics of anion exchange of NO₃⁻ in Zn-Al-NO₃ hydrotalcite by dichromate is fit to the second order of reaction to yield reaction rate constant $k = 0.301 \text{ M}^{-1} \text{ s}^{-1}$ ($R^2=0.95$). The anion exchange capacity (AEC) was observed to be 381 meq Cr₂O₇²⁻/100 g hydrotalcite. Further, the Zn-Al-Cr₂O₇ hydrotalcite could be regenerated successfully by NO₃⁻.

Keywords: hydrotalcite, nitrate, anion exchange capacity, dichromate, regeneration

INTRODUCTION

Chromium is of crucial importance because of its use in stainless steel and superalloys. These materials are vitally important to industrialized societies because of their applications in jet engines, nuclear plants, chemical-resistant valves, and other applications in which a material that resist heat and chemical attack is required. However, chromium waste can be dangerous for environment because its forms are determined as toxic metal. Species of Cr(VI) in water system can be very toxic, corrosive, and carcinogenic and have high dissolving. Dissolved oxygen in water system can slowly oxidize Cr(III) to Cr(VI) and gives effect for mortality. The maximum permitted limit of chromium in fresh water is 0.05 mg/L. This toxicity can result in lungs cancer and chronics injury [1]. Chromium(VI) in water system has two forms; those are Cr₂O₇²⁻ and CrO₄²⁻ anions [2]. Although waste treatment can be done using precipitation method yet the effectiveness needs to be investigated more.

Chromium exists in the oxidation states ranging from +6 to -2, however, only the +6 and +3 oxidation states are commonly encountered in the environment. Cr(VI) exists in solution as monomeric ions H₂CrO₄, HCrO₄⁻, and CrO₄²⁻ (chromate), or as the dimeric ion Cr₂O₇²⁻

(dichromate). Significant concentrations of H₂CrO₄ only occur under the extreme condition of pH 1 or lower. Above pH 6.5, CrO₄²⁻ dominates. Below pH 6.5, HCrO₄⁻ dominates when the Cr(VI) concentrations are low (<40 mM); but Cr₂O₇²⁻ becomes significant when concentrations are greater than 1 mM, or it may even dominate when the total Cr(VI) concentrations are greater than 30 mM. In the Cr(III)-H₂O system, Cr(III) exists predominantly as Cr³⁺ below pH 3.5. With increasing pH, hydrolysis of Cr³⁺ yields CrOH²⁺, Cr(OH)₂⁺, Cr(OH)₃, and Cr(OH)₄⁻ [4].

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, are two dimensional layered materials. The best known of these materials is hydrotalcite, Mg₆Al₂(OH)₁₆(CO₃)·4H₂O, whose structure is derived from the brucite Mg(OH)₂ [5]. Anionic clays, such as hydrotalcites, are not as well known and rare in nature than cationic clays such as smectites. The first hydrotalcite was discovered in Sweden around 1842. Anionic clays have a structure electrically opposite to that exhibited by cationic clays. Their structure can be derived from the brucite structure, Mg(OH)₂, where each Mg²⁺ ion is octahedrally surrounded by six OH⁻ ions. The hydrotalcite type (HT) structure is obtained when some of the Mg²⁺ ions, or other divalent cations, are replaced by trivalent cations, with a similar radius.

The higher charge of the trivalent cations imposes an overall positive charge on the brucite-type layer, which is compensated by the incorporation of generally hydrated interlayer anions (Figure 1). A wide range of compositions is possible for synthetic hydrotalcites, based on the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{b+} [A_n]_{b/n} \cdot mH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent cations in the octahedral positions within the hydroxide layers with x normally ranging between 0.17 and 0.33, A^n is an interlayer anion with a negative charge n , b is the charge of the layer and m is the number of water molecules. Many anions or anionic complexes, both organic and inorganic, can and have been incorporated into the hydrotalcite structure [6].

The wide range of materials of this type that can be synthesized gives rise to a range of applications including catalysts and catalyst precursors, ion exchangers and adsorbents, anion scavengers and stabilizers, etc. A comparative list of ion selectivity for monovalent anions as $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$, and for divalent anions $CO_3^{2-} > C_{10}H_4N_2O_8S^{2-} > SO_4^{2-}$. For oxoanions the order is $HPO_4^{2-} > HAsO_4^{2-} > CrO_4^{2-} > SO_4^{2-} >$

MoO_4^{2-} [3]. According to these guidelines, Zn-Al- NO_3 hydrotalcite are one of the best anion exchangers. Considering hydrotalcite ability to exchange its negative charge, hydrotalcite can be used as an anion exchanger. This ability can be used to treat liquid pollutant containing much anion pollutants which are more difficult to be handled and processed because of its difficulty to precipitate. A treatment using anion exchange is a common process yet it is usually more expensive. Therefore, hydrotalcite as an anion exchanger needs to be investigated more.

Hydrotalcite with high anion exchange capacity (AEC) and its ability to be regenerated are important to determine hydrotalcite for its application as anion exchanger. In our previous publication, we have reported about hydrotalcite Zn-Al- NO_3 as anion exchanger for pollutant treatment of hexacyanoferrate(II) [8]. This paper focuses on the hydrotalcite mechanism, capacity, and anion exchange kinetics by $Cr_2O_7^{2-}$ and aims to obtain information related to anion exchange mechanism, regeneration process and its anion exchange capacity.

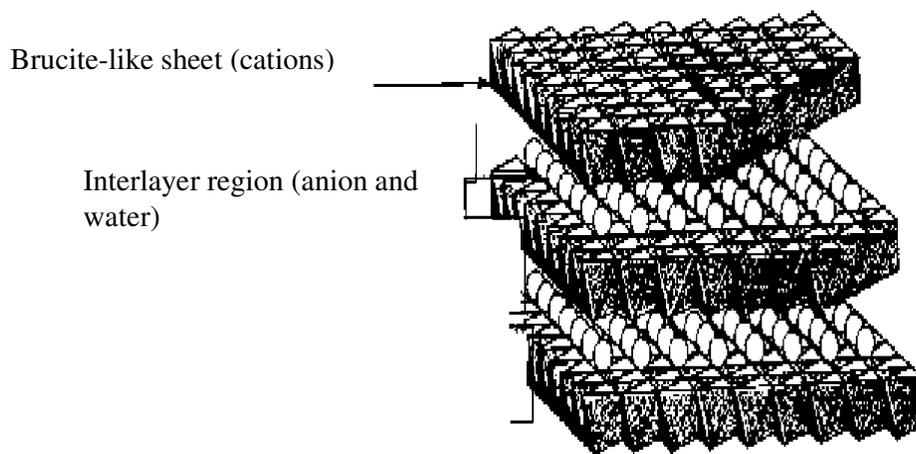


Figure 1. Structure of hydrotalcite [7]

EXPERIMENTAL

Synthesis and hydrotalcite characterization [9]

A 100 mL solution containing 0.30 M $Zn(NO_3)_2$ and a 100 mL solution containing $Al(NO_3)_3$ 0.10 M were prepared. Next, aqueous solution was titrated with vigorous stirring with a 100 mL NaOH 0.50 M. Nitrogen gas was purged into the mixture to reduce carbonate incorporation and the solution pH was maintained at 8. Hydrothermal treatment at 100 °C was done after 2

hour of stirring. Subsequently, the products were centrifuged, filtrated and washed. Obtained products were dried at 100 °C for 24 h, and the dried solids were crushed. Products were referred to as Zn-Al- NO_3 hydrotalcite.

Powder X-ray diffraction (PXRD) patterns of the samples were obtained with a Shimadzu Diffractometer XRD-6000. FT-IR spectra were recorded by a Shimadzu FT-IR-820 IPC. The Zn/Al ratio and anion capacity was determined by Perkin Elmer 3110 Atomic Adsorption Spectrophotometry.

Intercalation of $\text{Cr}_2\text{O}_7^{2-}$ in Zn-Al-NO_3 hydrotalcite

A portion of 0.10 g of the Zn-Al-NO_3 hydrotalcite was suspended in a 10 mL deionised water under nitrogen atmosphere for 30 minutes. Next, the amount of 0.30 g of $\text{K}_2\text{Cr}_2\text{O}_7$ suspended in a 10 mL deionised water was poured into Zn-Al-NO_3 hydrotalcite slurry also under nitrogen atmosphere for 2 hours where the molar ratio of NO_3^- to $\text{Cr}_2\text{O}_7^{2-}$ was adjusted to 1: 5 and pH was maintained at 6 using NaOH solution. After aging for 24 h at 100 °C the solid was centrifuged, filtered, washed, and dried at 75 °C for 20 h. The ion exchanged product was attributed as $\text{Zn-Al-Cr}_2\text{O}_7$ hydrotalcite and was subjected to the characterization using Shimadzu Diffractometer XRD-6000 and Shimadzu FT-IR-820 IPC.

After ion exchange, Cr^{6+} in the filtrate was determined using Perkin Elmer 3110 Atomic Adsorption Spectrophotometry to obtain the anion exchange capacity (AEC). A standard solution of Cr^{6+} was prepared by dissolving 0.0114 g potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 100 mL deionised water to give Cr^{6+} concentration of 25 mg/L. The stock solution was diluted to give Cr^{6+} concentrations of 4, 8, 12, 16, and 20 mg/L.

Kinetics study of anion exchange and regeneration process

Kinetics study was carried out by preparing five suspensions of 0.3 g Zn-Al-NO_3 hydrotalcite in 25 mL $\text{K}_2\text{Cr}_2\text{O}_7$ solution 0.06 M under nitrogen atmosphere. Each of suspension was stirred under nitrogen atmosphere for 60, 300, 900,

1800 and 3600 seconds. The hydrotalcite was separated by centrifugation. After each centrifuging process, the solid was washed repeatedly. The chromium in the supernatant was analyzed by atomic absorption spectrophotometry.

For the regeneration of hydrotalcite, a portion of 0.070 g $\text{Zn-Al-Cr}_2\text{O}_7$ was mixed with 25 mL solution of KNO_3 0.40 M under nitrogen atmosphere for 2 hours. Hydrothermal process at 100 °C for 15 hours was carried out. Later, the solid was separated and dried at 90 °C for 4 hours using air oven. The solid was characterized by Shimadzu Diffractometer XRD-6000 and Shimadzu FTIR-820 IPC.

RESULT AND DISCUSSION

Synthesis hydrotalcite Zn-Al-NO_3

Figure 2 shows the XRD pattern of Zn-Al-NO_3 hydrotalcite prepared using $\text{Zn}(\text{NO}_3)_2$ solution and $\text{Al}(\text{NO}_3)_3$ solution. Zn-Al-NO_3 hydrotalcite has basal spacing of $d_{003} = 8.83 \text{ \AA}$ [10] compared with basal spacing $d_{003} = 8.76 \text{ \AA}$ that appeared at diffraction angle of 2θ 10.08°. FT-IR spectra (Figure 3) shows that nitrate present in hydrotalcite interlayer space with strong and sharp absorption band at 1381 cm^{-1} and weak absorption band at 601 cm^{-1} . Absorption at 3456 cm^{-1} can be ascribed as stretching vibration mode of hydroxyl group of the hydrotalcite layers and water in interlayer gallery. Interlayer water molecules appeared at 1627 cm^{-1} and Zn-O-Al bonds appeared at 424 cm^{-1} .

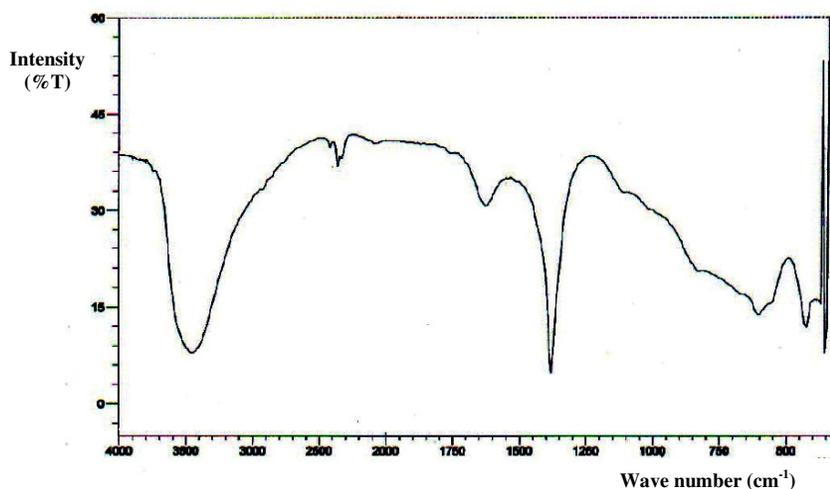


Figure 3. FT-IR spectra of Zn-Al-NO_3 hydrotalcite

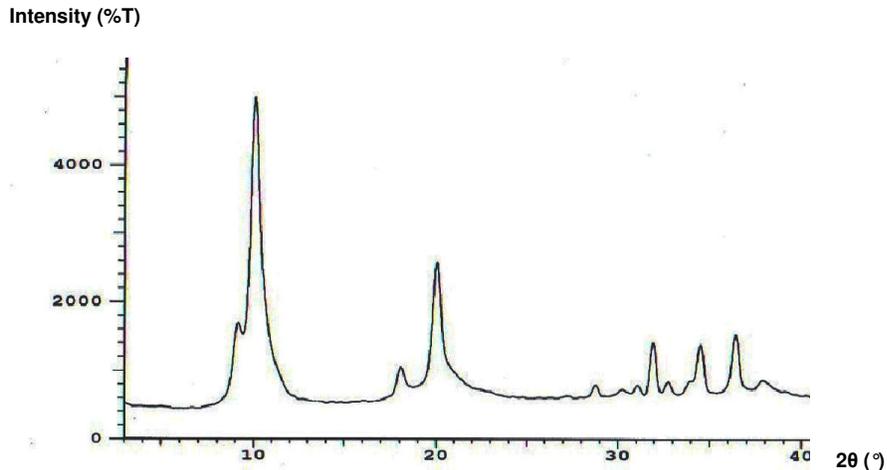


Figure 2. Difraktogram XRD of hydrotalcite Zn-Al-NO₃

Table 1. Chemical composition of hydrotalcite Zn-Al-NO₃

| Component | Composition | |
|------------------|-------------|-------------|
| | %b/b | Molar ratio |
| Zn | 48.0 | 0.74 |
| Al | 7.1 | 0.26 |
| H ₂ O | 5.0 | 0.30 |
| Ratio Zn/Al | 2.85 | |

Table 1 shows the chemical composition of Zn-Al-NO₃ hydrotalcite. The water content estimated approximately 1 to 4 moles for each mole of hydrotalcite. The hydrotalcite has chemical formula of Zn_{0.74}Al_{0.26}(OH)_{1.7}(NO₃)_{0.26}·0.27H₂O in which Zn/Al ratio of 2.85. The Zn to Al ratio was close to 3:1 as expected based on the composition of the starting solution.

Anion exchange of NO₃⁻ in Zn-Al-NO₃ hydrotalcite by Cr₂O₇²⁻ and its regeneration process

Figure 4 shows the XRD patterns of initial Zn-Al-NO₃ hydrotalcite, Zn-Al-NO₃ hydrotalcite after anion exchange with Cr₂O₇²⁻ and Zn-Al-NO₃ hydrotalcite after regeneration. The XRD patterns of the Zn-Al-NO₃ hydrotalcite after anion exchange with Cr₂O₇²⁻ shows an increase in basal spacing from 8.76 Å to 10.04 Å indicating that intercalation of the dichromate anion occurred. XRD patterns also show that nitrate can easily regenerate dichromate as shown by the peak of diffraction d₀₀₃ at 7.77 Å in presented in Table 2. Models for the orientation of dichromate in the LDH intercalates can be seen in Figure 5.

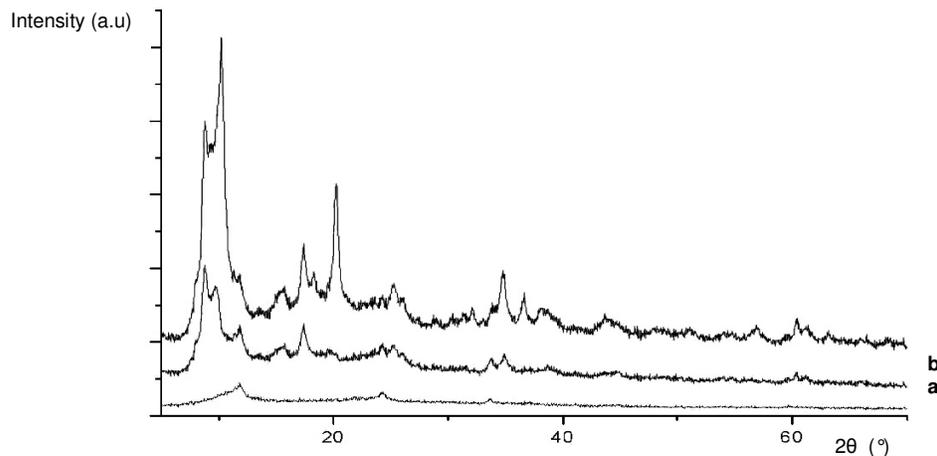


Figure 4. XRD pattern of (a) initial Zn-Al-NO₃ hydrotalcite, (b) Zn-Al-Cr₂O₇, and (c) Zn-Al-NO₃ regeneration

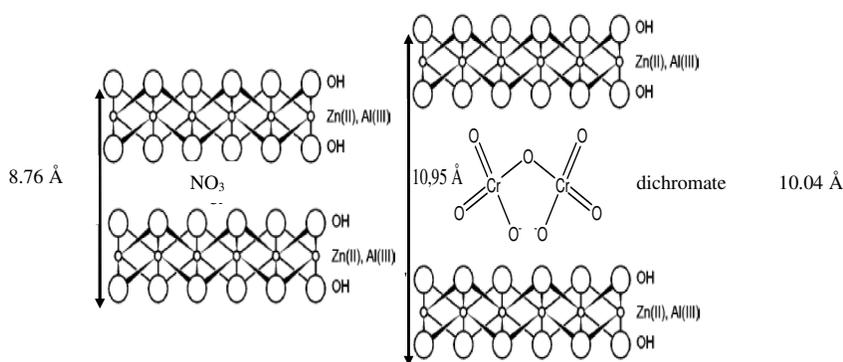


Figure 5. Models for the orientation of dichromate in the LDH intercalates

Table 2. Basal spacing data of Zn-Al-NO₃ hydrotalcite

| | Zn-Al-NO ₃ (initial) | Zn-Al-Cr ₂ O ₇ (anion exchange) | Zn-Al-NO ₃ (regeneration) |
|----------------------|------------------------------------|--|---|
| d ₀₀₃ (Å) | 8.76 | 10.04 | 7.77 |
| d ₀₀₆ (Å) | 4.42 | 9.11 | 3.67 |

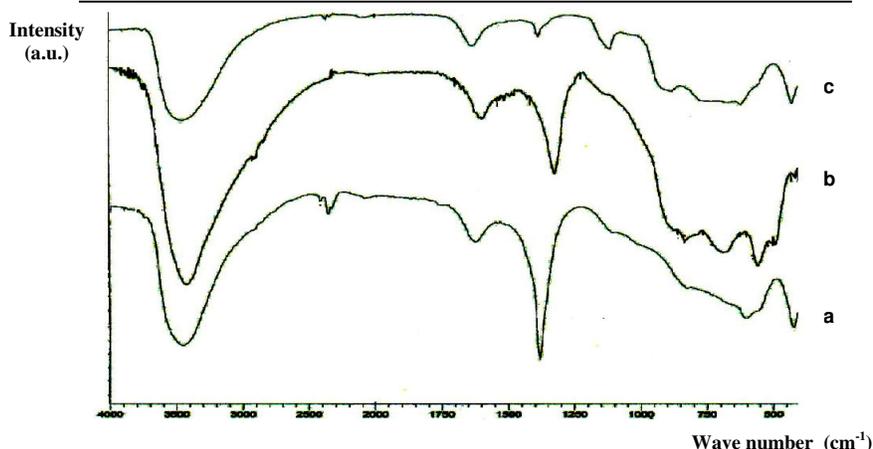


Figure 6. The FT-IR spectra (a) initial Zn-Al-NO₃ hydrotalcite (b) Zn-Al-Cr₂O₇, and (c) Zn-Al-NO₃ regeneration.

The FT-IR spectra of the pristine initial Zn-Al-NO₃ hydrotalcite (Figure 6) show a broad band at 3456 cm⁻¹ due to the OH stretching of water molecules and hydroxyl groups of the brucite layers, a narrower absorption band at 1627 cm⁻¹ due to H₂O vibration of the water molecules, a band at 1381 cm⁻¹ due to interlayer nitrate and a band at 424 cm⁻¹ as a characteristics of Zn-O-Al. The typical band of carbonate at 1360 cm⁻¹ confirms that a small amount of this anion is present in the interlayer space, probably through adsorption from atmospheric carbon dioxide, despite the precautions taken during preparation. This fact is not surprising because of the high affinity toward this anion by hydrotalcite. A broad band of OH stretching of water molecules and hydroxyl groups of the brucite layers at 3456 cm⁻¹ shift to 3433 cm⁻¹ and a band at 1381 cm⁻¹ due to interlayer nitrate disappearance. A

nitrate anion in hydrotalcite interlayer will reappear at 1381 cm⁻¹ indicating that regeneration process succeeded (Figure 6).

Kinetics of anion exchange of NO₃⁻ in Zn-Al-NO₃ hydrotalcite by Cr₂O₇²⁻

Anion exchange of Zn-Al-NO₃ hydrotalcite by Cr₂O₇²⁻ was kinetically studied by atomic adsorption spectrophotometry technique. Figure 7 shows the remained concentration of Cr₂O₇²⁻ in solution versus time (second). A good straight line was always obtained upon plotting 1/C versus time (Figure 7). The observed second order rate constants were inferred from the slope with reaction rate constant (k) = 0.301 M⁻¹s⁻¹ (R²) = 0.952.

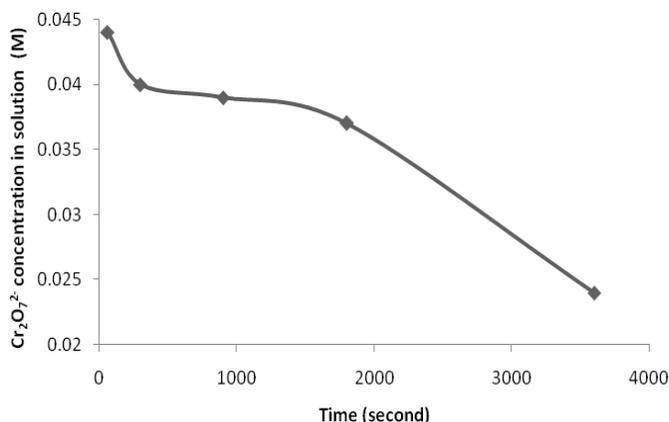


Figure 7. The progress of $\text{Cr}_2\text{O}_7^{2-}$ concentration reduction during ion exchange

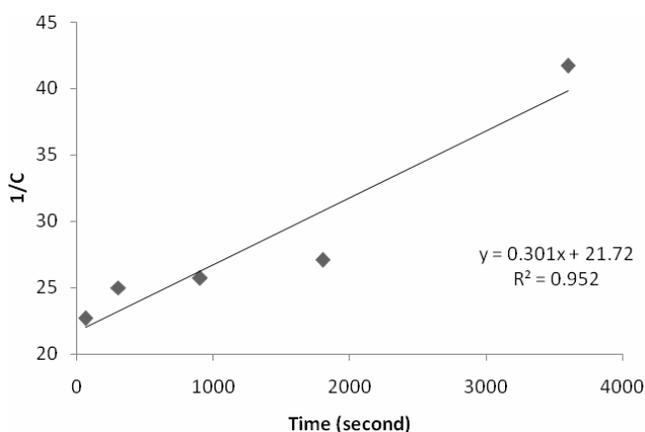


Figure 8. Plot of $1/C$ versus time for ion exchange reaction of Zn-Al- NO_3 by $\text{Cr}_2\text{O}_7^{2-}$.

Anion exchange capacity (AEC) of Zn-Al- NO_3 hydrotalcite with dichromate anion of 381 meq $\text{Cr}_2\text{O}_7^{2-}/100$ g much more than Zn-Al-Cl hydrotalcite with dichromate having anion exchange capacity of 216 meq $\text{Cr}_2\text{O}_7^{2-}/100$ g [11]. A comparative list of ion selectivity for anion exchanger was influenced by anion charge, electron density, and hydrogen bond [12].

CONCLUSION

The initial Zn-Al- NO_3 hydrotalcite having chemical formula $\text{Zn}_{0.74}\text{Al}_{0.26}(\text{OH})_{1.7}(\text{NO}_3)_{0.26} \cdot 0.27\text{H}_2\text{O}$ has been successfully synthesised and its application as an anion exchanger has been investigated. This high potency of Zn-Al- NO_3 hydrotalcite as an anion exchanger is evident where its anion exchange capacity (AEC) is 381 meq $\text{Cr}_2\text{O}_7^{2-}/100$ g. Kinetics of anion exchange of NO_3^- in Zn-Al- NO_3 hydrotalcite by dichromate is fit to the second order of reaction and yield reaction rate constant (k) of $0.301 \text{ M}^{-1}\text{s}^{-1}$ ($R^2=0.95$). The Zn-

Al- Cr_2O_7 hydrotalcite could be regenerated successfully when solution of potassium nitrate was used.

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